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Thema: **Hochtemperaturmassenspektroskopie**

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Wissenschaftliche Vorbereitung: K. G. Weil, Darmstadt

Hauptvorträge: E. W. Schlag, München: „Mehrphotonen-Ionisation für die Massenspektroskopie“  
 M. Irion, Irvine, California: „Fourier-Transform-Massenspektroskopie“  
 K. G. Weil, Darmstadt: „Der Dampf über intermetallischen Systemen“

Über neue Ergebnisse soll in Form von 20-minütigen Vorträgen berichtet und diskutiert werden. Arbeiten, in denen methodische Fortschritte angestrebt werden, sind ebenso willkommen wie solche, in denen chemische Prozesse oder Strukturen mit Hilfe der Massenspektroskopie aufgeklärt werden sollen.

Anmeldungen, denen eine Zusammenfassung von maximal einer Schreibmaschinenseite Umfang beiliegt, werden bis zum 15. August 1984 erbeten. Die Anmeldung der Teilnehmer sollte ebenfalls zu diesem Termin vorliegen. Allen Teilnehmern werden ein Programm, Unterlagen zur Zimmerbestellung sowie ein Lageplan des Tagungsgebäudes zugesandt.

Die Tagungsgebühr beträgt 30, – DM, für Doktoranden 15, – DM. Es wird gebeten, der Anmeldung einen Verrechnungsscheck beizulegen.

Anmeldungen und sonstige Korrespondenz bitte an Prof. Dr. K. G. Weil, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraße 20, D-6100 Darmstadt, Telefon: 061 51/162498.

Der 1. Vorsitzende  
 Prof. Dr. H. Gg. Wagner

## Infrared Spectrum of Isoselenocyanic Acid, HNCSe

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### *Chemical Kinetics / Molecular Interactions / Molecular Structure / Spectroscopy, Infrared*

The preparation of gaseous isoselenocyanic acid, HNCSe, first reported by Landsberg [10] in 1979, has been considerably improved. This unstable molecule decays in the gaseous phase according to a second-order reaction. In the infrared region the vibrational spectrum of HNCSe was measured in the gaseous phase and in an argon matrix at low resolution. The combined analysis of the vibrational spectra of HNCSe yielded the assignment of the A' fundamental vibrations. From the gaseous phase absorptions  $\nu_1 = 3535 \text{ cm}^{-1}$ ,  $\nu_2 = 1957 \text{ cm}^{-1}$  and  $\nu_3 = 625 \text{ cm}^{-1}$  could be assigned. The bands in the gas phase spectrum at 760, 583, 521 and  $419 \text{ cm}^{-1}$  cannot be considered as band centers. They are the result of the superposition of the subband structures of the bending modes  $\nu_4$ ,  $\nu_5$  and  $\nu_6$  exhibiting quasilinear behaviour. This can be deduced from the wavenumber positions of  $\nu_4 = 508 \text{ cm}^{-1}$  and  $\nu_5 = 419 \text{ cm}^{-1}$  observed in the argon matrix spectra. Due to the rapid H/D exchange the infrared spectrum of DNCSe could not be measured.

### Introduction

Isoselenocyanic acid, HNCSe, belongs to the very interesting group of homologs of isocyanic acid, HNCO, in which the terminal oxygen is replaced by sulfur or selenium. Although organic selenocyanates, RSeCN, and isoselenocyanates, RNCSe, are fairly well known [1], knowledge concerning the corresponding free acids is very limited due to their instability.

Berzelius [2] prepared the first potassium salt of these acids around 1820. The first aqueous solution of HNCSe was reported by Crookes [3] in 1852, who liberated the acid by treating an aqueous suspension of lead selenocyanate with hydrogen sulfide. It was impossible to concentrate this solution

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even over concentrated sulfuric acid or in vacuum without decomposing HNCSe into hydrogen cyanide and selenium. Since that time there have been several attempts to isolate HNCSe [4] or to prepare a reasonably stable solution in organic solvents [5]. Due to its instability in aqueous solutions the physical and chemical properties could only be determined indirectly. The acid strength for example was obtained by two different electrochemical methods [6, 7] and was found to be similar to that of isothiocyanic acid, HNCS. The autocatalytic decomposition of this strong acid was studied in aqueous solutions as a function of the pH value [8].

Until recently there was no direct proof of the existence of the free acid. Although infrared spectra of HNCSe and DNCSe were announced in a paper dealing with the infrared spectrum of the  $\text{SeCN}^-$  ion [9], these spectra were never published. In 1979 Landsberg in this laboratory observed for the first time the gaseous isoselenocyanic acid, HNCSe, by passing hydrogen bromide through a densely filled column of silver selenocyanate [10]. The resulting gas was analysed in a microwave spectrometer. By means of the spectral patterns of two rotational transitions, caused by the various selenium isotopes in natural abundance, HNCSe was unambiguously identified. Similar data were obtained for the DNCSe and  $\text{HN}^{13}\text{CSe}$  species so that a preliminary  $r_s$ -structure could be determined. Moreover, the  $^{14}\text{N}$  hyperfine structure and the dipole moment component  $\mu_a$  were determined, further supporting the HNCSe structure. As in the case of HNCO and HNCS the other tautomer HSeCN was not observed.

Some aspects of the quasilinear behaviour of isoselenocyanic acid, HNCSe, will be described in a following paper [11], where we report the further measurements of the rotational spectrum and a revised substitution structure of the molecule. In this paper we present an improved preparation method, a study of the decomposition kinetics of this unstable species in the gaseous phase and its low resolution infrared spectra from 400 to  $4000\text{ cm}^{-1}$  in the gaseous phase and in matrix isolation.

## 2. Experimental Procedures

In order to produce adequate amounts of gaseous HNCSe, alternative syntheses of the molecule were tried. Among these alternatives was the attempt to prepare HNCSe by the pyrolysis of selenourea in analogy to a well known preparation of HNCO [12]. Since HNCSe could not be chemically isolated, as mentioned above, only reactions with rather simple byproducts were investigated, whose spectra could not seriously interfere with the infrared or millimeter wave spectra of HNCSe.

A modification of the original method of synthesis [10] was thus finally employed. Instead of passing a gaseous mixture of 0.2 kPa HBr and 50 kPa dry nitrogen through a narrow packed column of silver selenocyanate, AgNCSe, a fluid-bed reactor was used. AgNCSe was prepared by a precipitation reaction of aqueous silver acetate with ethanolic potassium selenocyanate solution [13] and dried in vacuum. The HBr (Merck-Schuchardt) was purified by two sublimations at low temperature in vacuum.

In the modified optical arrangement of the Digilab FTS 20B used in our experiments the infrared source, a Nernst glower, was removed from the spectrometer compartment and was installed on an adjustable stand about 3.10 m away. The 3 m absorption cell was positioned between the radiation source and the interferometer. In order to reduce wall decomposition of HNCSe the cell was conditioned prior to the measurements by filling it several times with a few 100 Pa of HNCS which polymerises within a day at room temperature. The resulting polymer film on the glass walls considerably slowed the rate of decomposition of HNCSe.

The instability of HNCSe allowed only spectra with a resolution of 4 or  $1\text{ cm}^{-1}$  to be recorded. In order to obtain a reasonable signal-to-noise ratio, especially in the finger-print region below  $1000\text{ cm}^{-1}$  where weak bands are located, 50 interferograms were collected. After refilling the cell further interferograms were taken and coadded to those of the first filling. This procedure was repeated until selenium on the windows and in the reactor reduced the signal-to-noise ratio substantially, before finally the resulting interferogram was Fourier transformed. In order to compensate the resulting single-beam spectra, a comparable number of interferograms was collected, coadded and Fourier transformed after the cell had been evacuated.

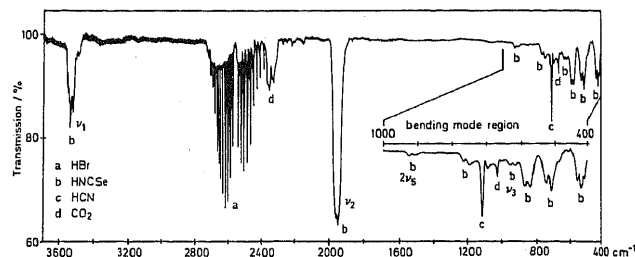


Fig. 1

Infrared spectrum of gaseous HNCSe with the assignment indicated (500 scans,  $1\text{ cm}^{-1}$  resolution, 10 fillings in a 3 m glass absorption cell at about 40 kPa total pressure)

The mid-infrared spectrum of HNCSe is shown in Fig. 1, which was obtained from ten cell fillings and from a total of 500 coadded scans. HNCSe can be identified by the very strong band at  $1957\text{ cm}^{-1}$ , which was used for kinetic studies as discussed above, and by the NH stretching vibration at  $3535\text{ cm}^{-1}$ , which are consistent with the conformation HNCSe obtained previously in the microwave region by Landsberg [10]. The decomposition product HCN can be identified by its bending mode at  $710\text{ cm}^{-1}$ .

Since only small amounts of substance are needed for matrix isolation spectroscopy, HNCSe was prepared by passing HBr, diluted with dry argon in a ratio of 1:500, through a packed column of AgNCSe. The resulting gas mixture was deposited on a CsI substrate window, cooled by a closed-cycle helium cryostat to 10 K. For recording the spectra with a resolution of  $0.25\text{ cm}^{-1}$  the cold head with the substrate was placed in the conventional sample compartment, which allowed the Fourier transform spectrometer to be operated in its original optical configuration. Only single-beam spectra could be obtained. In order to compensate the background, a single-beam spectrum was recorded after the matrix had been photolysed with ultraviolet light for two hours. The two single-beam spectra were digitally ratioed by the computer, and the resulting spectrum, which looks very clean, is shown in Fig. 2. Due to the ratioing only bands belonging to

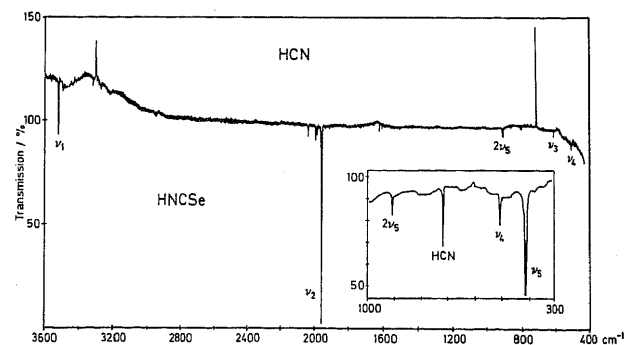


Fig. 2

Infrared matrix isolation spectrum of HNCSe in an argon matrix at 10 K ( $M:A = 1:500$ ) recorded with a Fourier transform spectrometer. In the inset on the right the spectrum is displayed which was observed with a grating spectrometer. Due to ratioing of single beam spectra of the original and of the irradiated matrix only the instable molecule HNCSe is displayed in the normal transmission range, whereas the bands of the photolysis product are pointing upward

the unstable molecule HNCSe appear in absorption. The molecule can easily be photolysed and these distinctive bands disappear. The features pointing to higher transmission belong to the photolysis product HCN. Since stable compounds are present both in the original matrix and the irradiated matrix and are insensitive to irradiation, their bands totally compensate.

### 3. Kinetic Studies of HNCSe Decomposition

In order to obtain IR spectra with a reasonable signal-to-noise ratio it was necessary to have some knowledge of the lifetime of HNCSe under the prevailing experimental conditions. Landsberg [10] determined the lifetime of HNCSe in a gold-plated microwave cell to be about 90 seconds. Since metals catalyse the decomposition only glass absorption cells were employed in the present study, and the decay kinetics of HNCSe was thus studied in a glass vessel. HNCSe was produced as described above and released into a 3 m glass cell equipped with KBr windows. In order to follow the HNCSe decay the infrared absorption spectrum of the gas mixture was recorded at low resolution at defined time intervals.

The decomposition follows a second-order rate equation which implies that the decrease  $x$  of the HNCSe concentration with time  $t$  is proportional to the square of the instantaneous amount of HNCSe:



$$-\frac{dx}{dt} = k(a-x)^2. \quad (2)$$

Since the absolute concentration of HNCSe cannot be determined in the gas mixture, the intensity of  $\nu_2$ , which is the most intense band in the infrared spectrum, has been taken as a relative measure for the concentration of HNCSe. Thus, in the modified integrated second-order rate equation Eq. (3)  $A$  represents the area of the  $\nu_2$  band at time  $t$ , whereas  $A_0$  is the area at the beginning of the measurement:

$$\frac{1}{A} - \frac{1}{A_0} = k't. \quad (3)$$

When the differences of the reciprocal band areas are plotted versus time, as shown in Fig. 3, the plotted measurements follow fairly well a straight line. The decomposition of HNCSe thus represents a second-order reaction. As soon as the glass walls are coated with selenium, this simple equation is no longer valid.

A similar kinetic relationship was obtained in the glass absorption cell of a millimeter wave spectrometer [11]. Since much smaller concentrations of HNCSe are necessary for the observation of rotational spectra, HNCSe could be prepared at about 2.5 Pa total pressure without a carrier gas. The gases were released into a 3 m free space cell and monitored by the rotational absorption lines of HNCSe. When the reciprocal height of a particular line is plotted versus time, again a straight line results. That means that the carrier gas does not stabilise HNCSe, but serves to produce greater amounts of HNCSe in the cell by removing it rapidly from the reaction zone.

In general sufficient HNCSe is still present for 20 to 30 minutes after filling the cell to perform spectroscopic studies.

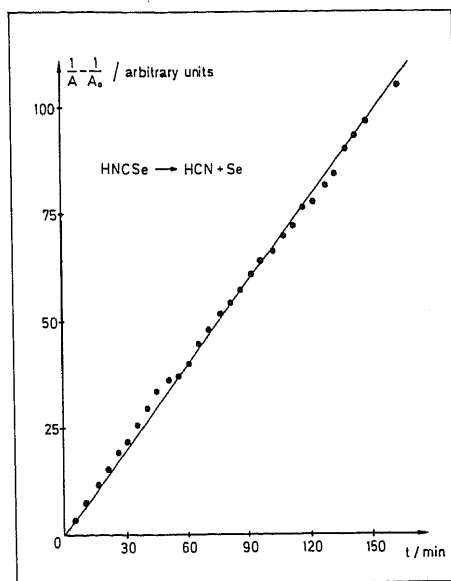


Fig. 3

Decay of HNCSe in the gaseous phase as a function of time in the glass absorption cell. The decay follows a second order reaction.  $A$  is the area of the fundamental band  $\nu_2$  and  $A_0$  the area at  $t = 0$

The fact that even three hours after the initial production HNCSe can still be detected is due to the great intensity of the vibrational band  $\nu_2$ .

### 4. Vibrational Spectrum of HNCSe and its Interpretation

Since HNCSe belongs to the point group  $C_s$ , there are five in-plane ( $A'$ ) and one out-of-plane ( $A''$ ) fundamental vibrations, the assignments of which are listed in Table 1. The vibrational assignment of the gas phase spectrum was found in combination with the matrix isolation spectrum.

Table 1  
Infrared bands of isoselenocyanic acid, HNCSe, in  $\text{cm}^{-1}$  observed in the gaseous phase and in a cryogen argon matrix

Mode	Gas	Matrix
$\nu_1$	3535	3516.4
$\nu_2$	1957	1957.9
$2\nu_5$	917	908.3
$\nu_3$	625	617.6
$\nu_4$	— <sup>a)</sup>	508.3
$\nu_5$	— <sup>a)</sup>	419
$\nu_6$	— <sup>a)</sup>	—

<sup>a)</sup> The bands in the gas phase spectrum at 760, 583, 521 and 419  $\text{cm}^{-1}$  cannot be regarded as band centers, but result from the subband structures of the bending modes  $\nu_4$ ,  $\nu_5$ , and  $\nu_6$  (see text).

In the matrix isolation spectrum the vibrations at 3516  $\text{cm}^{-1}$  and 1957  $\text{cm}^{-1}$  are rather strong, whereas there are weak bands at 908, 618, and 508  $\text{cm}^{-1}$ . Due to the cut-off of the spectral range caused by the optical components of the interferometer, only bands above 460  $\text{cm}^{-1}$  could be observed. Thus, the finger-print region was also investigated using a grating spectrometer which CsI optics. This result is also displayed in Fig. 2. At 419  $\text{cm}^{-1}$  there is a further absorption. The weak and

very narrow band at  $618\text{ cm}^{-1}$  could only be detected with the Fourier transform spectrometer, which has higher sensitivity and better resolution.

In matrix isolation spectra only vibrational transitions starting from the ground vibrational state can be observed, since higher vibrational states are scarcely populated at cryogenic temperatures. Consequently hot bands and difference bands cannot be expected in the matrix spectra.

The assignment of the two higher stretching vibrations was straight-forward and is listed in Table 1. The two strongest bands (Fig. 1 and 2) can be easily assigned to the NH and asymmetric NCSe (N–C) stretching vibrations  $\nu_1$  and  $\nu_2$ , respectively, whereas the symmetric NCSe (C–Se) stretching fundamental  $\nu_3$  is expected to lie in the crowded region of the bending modes. Comparing the homolog series OCX with X=O, S and Se the wavenumbers of the C–X stretching modes decrease with the substitution of the chalcogen from  $1388\text{ cm}^{-1}$  in  $\text{CO}_2$  [14] via  $859\text{ cm}^{-1}$  in OCS [14] to  $643\text{ cm}^{-1}$  in OCSe [15]. In the homolog series HNCX, isoelectronic with OCX, there should be the same tendency. As can be seen in Table 2 the wavenumbers of the symmetric NCX gas phase stretching fundamentals  $\nu_3$  go from  $1327\text{ cm}^{-1}$  in HNCO [16] via  $857\text{ cm}^{-1}$  in HNCS [17] to  $625\text{ cm}^{-1}$  in HNCSe. The matrix band corresponding to this assignment for HNCSe is the weak band at  $618\text{ cm}^{-1}$ . In HNCO there is similarly good agreement between the gas phase and matrix assignment. Only in the case of isothiocyanic acid, HNCS, is there a large discrepancy, where the published matrix wavenumber of  $\nu_3$  is  $988\text{ cm}^{-1}$ . This problem has recently been reviewed in Ref. [18]. Since  $\nu_3$  is a very weak band in all these molecules as can be seen in Fig. 2 for HNCSe and in the published matrix isolation spectrum of HNCO [19], it was probably difficult to identify it in the matrix isolation spectrum of HNCS [20]. The assignment originally given for the matrix spectrum of HNCS should therefore be altered. The matrix band at  $988\text{ cm}^{-1}$  can be assigned either to an overtone or a combination band as discussed below. With enhanced resolution and sensitivity the very weak stretching fundamental  $\nu_3$  of HNCS should be detectable in matrix isolation using modern equipment nowadays.

The assignment of the bending modes was somewhat problematic due to their all lying close together, leading necessarily to serious perturbations caused by Coriolis resonances which are well studied in the cases of the lighter homologs HNCO [16]

and HNCS [17]. The in-plane bands should have band contours of A, B-hybrid bands in the gas phase spectrum, whereas the out-of-plane band should show the contour of a C-type band. The band contours of these perpendicular bands result from the superposition of subbands dominated by Q-branches, which are separated in the unperturbed case by  $2A$ , where  $A$  is the rotational constant with respect to rotation about the principal axis with the least moment of inertia. In the case of HNCO [16] and HNCS [17] the vibrational assignment was made possible by the rovibrational analysis of the high resolution gas phase spectra of these compounds; only on this basis the complicated band contours could be explained. In the case of HNCSe the band contours of the bending modes look much simpler. This must be due to the very large separation of the subbands ( $A$  is about  $57\text{ cm}^{-1}$ ; see Ref. [11]) and the consequently weak population of the substates for  $K_a > 0$ , which results from the very small least moment of inertia. Therefore the band contours and observable features in our spectrum cannot reflect directly the band centers of the bending modes. The assignment of the in-plane bending modes  $\nu_4$  and  $\nu_5$  in HNCSe can only be given unambiguously for the matrix isolation spectrum shown in Fig. 2, which resembles the matrix spectra of HNCO [19] and HNCS [20].

As Fusina and Mills demonstrated for HNCO by means of an harmonic force field analysis [21] the fundamentals  $\nu_4$  and  $\nu_5$  cannot be labeled as either HNC-bend and NCO-bend or vice versa. Instead of such labeling  $\nu_4$  should be regarded as an out-of-phase and  $\nu_5$  as an in-phase combination of the two bending coordinates, which give rise to the quasilinear behaviour of this molecule. A similar mixing of the normal coordinates can be expected for HNCS and HNCSe. Since the large-amplitude motion of the HNC valence bend contributes to both of these modes the observed differences between the gas phase and matrix wavenumbers could possibly be explained by matrix effects.

Comparing the relative intensities of  $\nu_4$  and  $\nu_5$  in the matrix spectra of HNCO [19], HNCS [20] and HNCSe there is a systematic change. Because there should be a bigger change of the dipole moment attributed by the HNC bending coordinate in comparison with the NCX bending coordinate, fundamentals with a high mixing ratio of the HNC bending coordinate should be more intense than bands with a high contribution from the in-plane skeleton bending coordinate. In the case of HNCO

Table 2  
Fundamental vibrations of pseudohalogen hydrazides HNX<sub>2</sub> in  $\text{cm}^{-1}$

Mode	HN <sub>3</sub>		HNCO		HNCS		HNCSe		Mode
	Gas <sup>a)</sup>	Matrix <sup>b)</sup>	Gas <sup>c)</sup>	Matrix <sup>d)</sup>	Gas <sup>e)</sup>	Matrix <sup>f)</sup>	Gas <sup>g)</sup>	Matrix <sup>h)</sup>	
$\nu_1$ $\nu_{\text{NH}}$	3336	3324	3531	3537.7	3538.6	3505	3535	3516.4	$\nu_1$ $\nu_{\text{NH}}$
$\nu_2$ $\nu_{\text{as}} \text{NXY}$	2140	2150	2274	2268.4	1989.0	1979	1957	1957.9	$\nu_2$ $\nu_{\text{as}} \text{NXY}$
$\nu_3$ $\nu_{\text{s}} \text{NXY}$	1274	1273	1327	1320.4	857.0	– <sup>h)</sup>	625	617.6	$\nu_3$ $\nu_{\text{s}} \text{NXY}$
$\nu_4$ $\delta \text{HNX}$	1150	1168	776.6	773.5	615.0	577	– <sup>h)</sup>	508.3	$\nu_4$ $\delta \text{NXY (A)}$
$\nu_5$ $\delta \text{NXY (A')}$	522	527	577.3	575.8	469.2	461	– <sup>h)</sup>	419	$\nu_5$ $\delta \text{HNX}$
$\nu_6$ $\delta \text{NXY (A'')}$	672	–	660	668.4	539.2	–	– <sup>h)</sup>	– <sup>h)</sup>	$\nu_6$ $\delta \text{NXY (A'')}$
$r(\text{NH})/\text{pm}$	101.5 <sup>i)</sup>		99.46 <sup>j)</sup>		99.28 <sup>k)</sup>		99 <sup>l)</sup>		$r(\text{NH})/\text{pm}$

<sup>a)</sup> Ref. [29]; <sup>b)</sup> Ref. [23]; <sup>c)</sup> Ref. [16]; <sup>d)</sup> Ref. [19]; <sup>e)</sup> Ref. [17]; <sup>f)</sup> Ref. [20]; <sup>g)</sup> This work; <sup>h)</sup> See text; <sup>i)</sup> Ref. [25]; <sup>j)</sup> Ref. [26]; <sup>k)</sup> Ref. [27]; <sup>l)</sup> Ref. [11].

[19]  $\nu_4$  is slightly more intense than  $\nu_5$ , whereas in HNCS [20] the situation is inverted. This interpretation is supported by the wavenumber dependence of these fundamentals on deuteration, which was discussed for HNCS in Ref. [17]. In the case of HNCSe  $\nu_5$  gains further in intensity at the expense of  $\nu_4$ , indicating an even larger participation of the HNC-bend in the  $\nu_5$  normal coordinate.

Unfortunately the band contours in the gas phase spectra gave no clear hint concerning the assignment of the out-of-plane vibration  $\nu_6$ . For a molecule which is so slightly asymmetric, B and C band contours are indistinguishable. Comparing the spectrum of HNCSe with those of  $\text{HN}_3$ , HNCO, and HNCS it is observed that the fundamental  $\nu_6$  is very weak or is even missing in the matrix. In the gaseous phase, however, these vibrations have similar intensities as the in-plane vibrations  $\nu_4$  or  $\nu_5$  due to Coriolis interactions. These phenomena have been found for  $\text{HN}_3$  [22, 23], HNCO [16, 19, 24], and HNCS [20]. In HNCS the  $\nu_6$  absorption is closely interwoven with that of  $\nu_4$  and  $\nu_5$  and could not possibly be identified from low resolution data. Although  $\nu_6$  of HNCSe cannot be observed in the matrix or assigned in the low resolution gas phase spectrum it can be predicted due to symmetry arguments to lie between the two bending modes  $\nu_4$  and  $\nu_5$  as in the case of  $\text{HN}_3$ , HNCO and HNCS (see Table 2).

In the matrix isolation spectrum of HNCSe (Fig. 2) the band at  $908\text{ cm}^{-1}$  cannot reasonably be assigned as a fundamental. Since this molecule belongs to the group of quasilinear molecules, which exhibit very anharmonic bending modes, this band can be regarded as the overtone of the fundamental  $\nu_3$  at  $419\text{ cm}^{-1}$ . In a typically quasilinear molecule such as fulminic acid, HCNO, the overtone of the anharmonic fundamental  $\nu_5$  was observed at about  $560\text{ cm}^{-1}$  in matrix spectra, whereas the fundamental can be seen at  $239\text{ cm}^{-1}$  [19]; the overtone lies considerably higher than twice the fundamental. The assignment of the matrix isolation spectrum of isothiocyanic acid, HNCS [20], shows a discrepancy concerning the stretching vibration  $\nu_3$  as mentioned above. As we now know HNCS is also a quasilinear molecule. Therefore we believe that the assignment of the matrix spectrum should be modified and the band at  $988\text{ cm}^{-1}$  is the overtone of  $\nu_3$  at  $461\text{ cm}^{-1}$ . Draper and Werner assigned the corresponding gas phase band to  $\nu_5 + \nu_6$  [17], but we find the overtone the more probable assignment.

Comparing the fundamentals of the four pseudohalogen hydrides  $\text{HN}_3$ , HNCO, HNCS and HNCSe as we have done in Table 2, it can be seen that the observed NH internuclear distances [11, 25–27] and the NH stretching wavenumbers  $\nu_1$  correlate in accordance with Bernstein's rule [28]. Following the series from  $\text{HN}_3$  to HNCSe all of the other fundamental vibrations are lowered successively. In  $\text{HN}_3$ , a typically bent molecule,  $\nu_4$  reflects the HNN bending mode, whereas in HNCSe, the most quasilinear molecule in this series,  $\nu_5$  represents closely the HNC bending coordinate. Between these

two limiting cases there is a change in the mixing ratio of the respective bending coordinates contributing to  $\nu_4$  and  $\nu_5$ . This change is indicated by the last column in Table 2, giving an alternative valence coordinate labeling of the normal modes.

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